ANL-6742

Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part I. The Fluorination of Uranium Dioxide-Plutonium Dioxide Solid Solutions

by

R. L. Jarry, L. J. Anastasia,
J. Fischer, L. E. Trevorrow,
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On page 5, 9th line from bottom should read:

"10,000 Mwd/ton burnup. . . ."

instead of "100,000 Mwd/ton burnup. . . ."

Alvin Glassner
Technical Publications Department

November 1, 1963

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for Plutonium and Uranium
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AEC Research and
Development Report

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Chemical Engineering Division

September 1963

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FOREWORD

This report is the first in a series of reports which will be issued from time to time under the general heading Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. These laboratory investigations will be concerned with various aspects of the processes and will be made to provide information that is needed for the design and operation of a pilot-plant facility.

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ABSTRACT

The experimental work reported herein has been performed in support of the development of fluid-bed fluoride volatility processes. In these processes, uranium and plutonium in spent nuclear fuels are converted into hexafluoride compounds in a fluid-bed reactor. The uranium and plutonium hexafluorides are volatile and can be separated from fission products, cladding, and alloying materials by techniques such as vaporization and distillation. The experimental work has been directed toward devising a fluorination procedure for uranium and plutonium dioxides which would result in a high degree of removal of uranium and plutonium as hexafluorides. In these experiments synthetic mixtures made up to simulate a charge for a fluidized bed reactor (100 kg U, 0.4 kg Pu, ~1 kg F.P., and 30 kg inert solids) were used.

High-purity recrystallized alumina was found to be a suitable material for use as the fluidized inert solid. After a 10-hr fluorination period at 450 C, the concentrations of residual uranium and plutonium on the alumina were 0.01 and 0.03 w/o, respectively. A reaction temperature of 450 C was found to be optimum, since experiments at 500 and 550 C resulted in plutonium retentions on the alumina of 0.060 and 0.090 w/o, respectively. At all these temperatures, the residual uranium content of the residue was less than 0.01 w/o. When fission product element oxides, in quantities that would be expected in a Dresden-type fuel after 100,000 Mwd/ton burnup and 30 days of cooling, were added to the uranium dioxide-plutonium dioxide-alumina and the mixture was fluorinated at 450 C for 10 hr, the concentration of plutonium on the alumina increased to a value of 0.065 w/o. Additional recovery of the plutonium retained on the alumina was obtained by either pyrohydrolysis followed by refluorination at 450 C for 10 hr, or by refluorination alone at 550 C for 10 hr. These procedures reduced the residual plutonium content of the alumina to less than 0.02 w/o.

Experiments were also performed to determine the feasibility of using the same batch of alumina as the inert solid for the fluorinations of five batches of the urania-plutonia solid solution. The recycle use of alumina did not result in a greater removal of plutonium than that which would have resulted if a fresh batch of alumina had been used with each batch of the uranium-plutonium oxide mixture.

Experiments were performed in which the solid solution of plutonium dioxide in uranium dioxide was oxidized prior to fluorination. The oxidation resulted in a powdered mixture of uranosic oxide and plutonium dioxide. Fluorination of this oxide mixture in alumina resulted in the removal of essentially all of the uranium in a reaction time of 2 hr at 450 C when 10 v/o fluorine was used. When this fluorination was followed by a second fluorination period of 5 hr at 550 C with 75 v/o fluorine, the plutonium content of the alumina was 0.011 w/o. When both fluorination periods were extended to 10 hr each, the retention of plutonium was 0.007 w/o, which corresponded to a removal of 99.5 percent of the plutonium contained in the solid mixture.

During the first part of the fluorination period, in which the major portion of the uranium is removed from the mixture of uranium dioxide, plutonium dioxide, alumina, and representative fission product element oxides, a low temperature (450 C) and a low concentration of fluorine (10 v/o fluorine in nitrogen) is desirable. However, in order to remove the plutonium efficiently during the last portion of the fluorination period, it is desirable to use a higher temperature (550 C) and a higher fluorine content of the gas mixture (75 v/o fluorine in nitrogen).

I. INTRODUCTION

Fluid-bed fluoride volatility processes[1] are being developed for the recovery of both uranium and plutonium from spent nuclear fuels. High-density uranium dioxide pellets, clad in either Zircaloy or stainless steel, are typical of the fuels that are amenable to purification by these processes.

A conceptual flowsheet for a fluid-bed fluoride volatility process is shown in Figure 1. In this process, the declad fuels are converted to fluoride compounds by a series of gas-solid reactions at elevated temperatures. The reactions are carried out while the fuel elements are immersed in a bed of inert solid. The granules of inert solid are fluidized by the reactant gases and provide a heat transfer medium for temperature control. The declad fuel elements are reacted with fluorine at about 500 C to convert the uranium and plutonium oxides to the volatile hexafluorides. Most of the fission products remain as nonvolatile fluorides in the inert solid bed, which is discarded as solid waste. The plutonium hexafluoride

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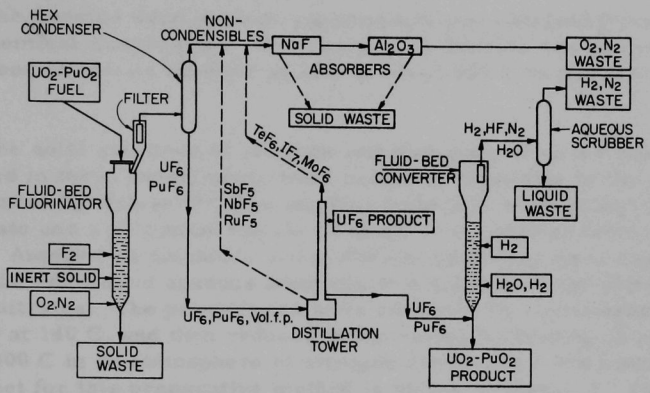
A conceptual flowsheet for a fluid-bed fluoride volatility process is shown in Figure 1. In this process, the decladed fuels are converted to fluoride compounds by a series of gas-solid reactions at elevated temperatures. The reactions are carried out while the fuel elements are immersed in a bed of inert solid. The granules of inert solid are fluidized by the reactant gases and provide a heat transfer medium for temperature control. The decladed fuel elements are reacted with fluorine at about 500 C to convert the uranium and plutonium oxides to the volatile hexafluorides. Most of the fission products remain as nonvolatile fluorides in the inert solid bed, which is discarded as solid waste. The plutonium hexafluoride

and uranium hexafluoride in the off-gas stream are condensed to solids in refrigerated traps. The components of this mixture of hexafluorides can be separated by fractional distillation or by selective thermal decomposition.(2) Uranium hexafluoride is very stable as compared with plutonium hexafluoride, which decomposes to plutonium tetrafluoride and fluorine.(3-5)

Figure 1

CONCEPTUAL FLOWSHEET FOR A
FLUID-BED FLUORIDE VOLATILITY PROCESS



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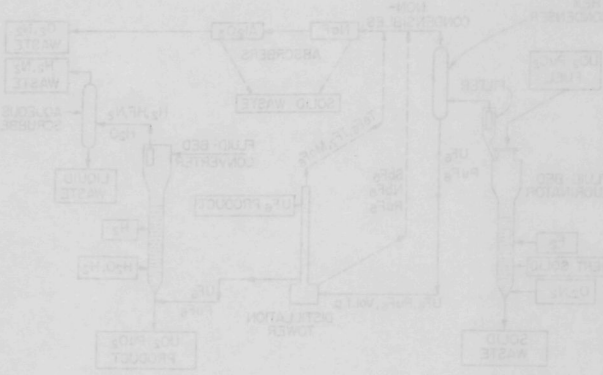
Since the inert solids will be discarded as waste, it is important for economic reasons that very little of the uranium and plutonium be retained on the solids after fluorination. The effect of plutonium retention on the economy of the fuel cycle can be illustrated by the following example: The charge from a power reactor, such as the Dresden Reactor, will probably consist of 100 kg of uranium, 400 g of plutonium, and about one kg of fission products. This charge will be mixed with about 30 kg of inert solid as the fluidized medium. The current processing scheme calls for processing a charge every 2 days. Therefore, on the basis of a 300-day working year, the loss of one percent of the plutonium would mean a total loss of 600 g/yr. If the value of the plutonium is assumed to be about $10 per gram, the total loss would amount to $6000 per year. This estimate is based on the practice of discarding the inert solids after each fluorination.

The experimental work presented in this report has been directed toward devising a fluorination procedure which would be applicable to fluid-bed fluoride volatility processes and which would result in the optimum removal of uranium and plutonium as their hexafluorides. In this work, synthetic mixtures were used to simulate the composition of the material



that will be charged to the fluid-bed reactor in plant operations. Experiments were performed to select a suitable inert solid, to determine the optimum temperature, time, and fluorine concentration for the reaction, to study the effect of fission product elements on the retention of plutonium on the inert solid, and to investigate the effect of prior oxidation on the reactivity of the uranium dioxide-plutonium dioxide mixture.

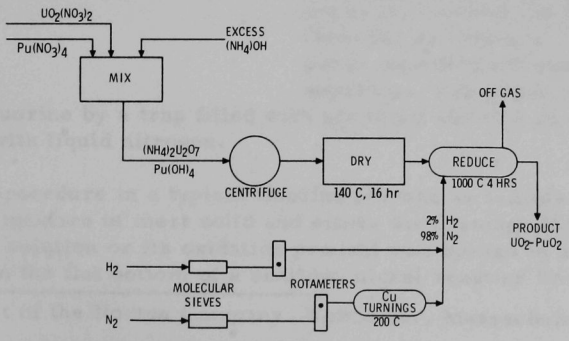
II. MATERIALS, APPARATUS, AND PROCEDURE

The fluorine used in these experiments was obtained from the Allied Chemical Corporation. Before use, the fluorine was passed through a heated bed of sodium fluoride pellets at about 100 C to remove hydrogen fluoride.

The solid solutions of uranium and plutonium dioxides which were fluorinated in these experiments were prepared according to the procedure recommended by Wilson.(6) The starting materials were uranyl nitrate hexahydrate and a plutonium nitrate solution, both obtained from AEC sources. Ammonium diuranate and plutonium hydroxide were coprecipitated by the addition of aqueous ammonia to a solution of the plutonium and uranium nitrates. The precipitates were collected by centrifugation, dried overnight at 140 C, and then reduced to the oxides by heating at a temperature of 1000 C in an atmosphere of nitrogen containing 2 v/o hydrogen. A flowsheet for this preparative method is shown in Figure 2. The oxide mixture was ground to a fine powder before use.

Figure 2

FLOWSHEET FOR THE PREPARATION OF URANIUM DIOXIDE-PLUTONIUM DIOXIDE SOLID SOLUTIONS



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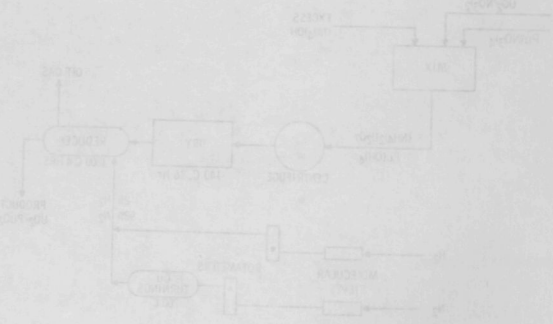
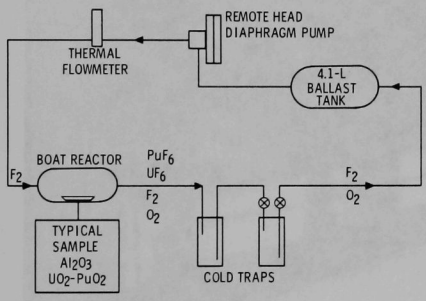


Several inert substances were tested to determine their suitability as inert solids. Two grades of recrystallized alumina were used: Type RR Alundum* (Blue Label) with a purity of 99.9+ percent alumina, and Type 38 Alundum* with a purity of 99+ percent alumina. Spectrochemical analyses showed the following impurities (expressed in ppm) for the Type 38 Alundum: Fe, 300; Mg, 400; Na, 2000; Si, 800; Ti, 400; and Zr, 400; the impurity level for the Type RR Alundum was less than or equal to 100 ppm for the same elements. Other inert solids studied were zirconium tetrafluoride, calcium fluoride, and aluminum fluoride. These substances were obtained from commercial sources and the purity of each was about 99 percent. Nickel fluoride, prepared by the fluorination of nickel chloride, was also tested.

Oxides of the fission product elements were commercially obtained** and had stated purities of greater than 99 percent.

Figure 3

SCHEMATIC DIAGRAM OF EQUIPMENT FOR URANIUM-PLUTONIUM FLUORINATION EXPERIMENTS



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The apparatus used in this work was assembled in a glovebox of the type described by Malecha et al.[7] Figure 3 is a schematic diagram of the fluorination apparatus, which was constructed of nickel and Monel; Figure 4 is a photograph showing one face of the glovebox. The apparatus included a horizontal tubular reactor, in which a nickel boat containing the solid sample was placed, a ballast volume of about 4 liters, a diaphragm pump† for circulating the gas phase, a thermal flowmeter[8] for sensing the flow rate, and cold traps to condense and remove the hexafluorides from the gas stream. A mechanical pump, provided for evacuation of the apparatus, was protected from fluorides and fluorine by a trap filled with activated alumina as well as by a trap cooled with liquid nitrogen.

The procedure in a typical fluorination was as follows: A weighed quantity of a mixture of inert solid and either the uranium dioxide-plutonium dioxide solid solution or its oxidation product was spread in a layer, $\frac{1}{32}$ to $\frac{1}{8}$ in. deep, on the flat bottom of a shallow, nickel reaction boat, the bottom

*Product of the Norton Company, Worcester, Massachusetts.

**American Potash and Chemical Corporation, West Chicago, Ill.

†Lapp Pulsafeeder No. CPS-1, Lapp Insulator Co., Inc., LeRoy, N.Y.

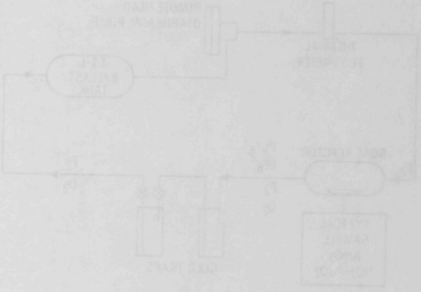

Figure 4

PHOTOGRAPH OF FLUORINATION EQUIPMENT
IN GLOVEBOX

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area of which was about 26 sq cm. The reaction boat was placed inside the horizontal, tubular reactor, and the system evacuated. When the reactor had reached the selected temperature, a fluorine-nitrogen mixture was admitted to the reaction system to a pressure of about one atmosphere, and the gas mixture was circulated over the sample at a rate of about 800 cc/min. The gas phase flowed in series across the surface of the solids in the tubular reactor, through two traps cooled in dry ice, through the diaphragm pump, through a thermal flowmeter, and, finally, back to the reactor. Uranium and plutonium hexafluorides which were formed in the reactor condensed and accumulated in the cold traps. At the end of a given fluorination period, the system was evacuated and filled with helium. After cooling, the reaction boat containing the residual solids was removed

from the tubular reactor and weighed. The entire solid residue was then dissolved in a sodium borate-sodium carbonate flux at 1000 C. The cooled resulting melt was dissolved in nitric acid. The solution was analyzed for uranium by fluorophotometric analysis. The plutonium content was determined by alpha counting after the plutonium had been extracted from the nitric acid solution with hexone in order to eliminate interference from americium. Because of the small quantity of plutonium used in each experiment, no attempt was made to collect the volatilized plutonium in order to obtain a material balance. Work covering the preparation, transport, and collection of plutonium hexafluoride has been previously reported.(5)

III. RESULTS AND DISCUSSION

An initial experiment was performed to determine the efficiency of fluorination of the uranium dioxide-plutonium dioxide solid solution. A sample of 9.95 g of the solid solution powder was placed on a thin nickel foil liner in the reaction boat and fluorinated for 10 hr at 450 C with 100 percent fluorine at a pressure of about one atmosphere. The nickel foil liner containing the residual uranium and plutonium was then dissolved in nitric acid and the solution analyzed. Only 0.21 mg of uranium and 0.12 mg of plutonium were found in the residue, representing 0.012 and 0.16 percent, respectively, of the quantities originally charged to the system. This result shows that the solid solution of plutonium dioxide in uranium dioxide does not in itself hinder the fluorination and removal of the uranium and plutonium hexafluorides.

Several materials were tested for use as the inert solid: recrystallized alumina (Alundum), nickel fluoride, zirconium tetrafluoride, and aluminum fluoride. The study of the inert fluorides was also of interest because they might appear in the reaction system as byproducts: nickel fluoride from the material of construction, zirconium tetrafluoride from residual quantities of zirconium remaining from a decladding step, and aluminum fluoride which would be present on the surface of the fluorinated recrystallized alumina.

The experiments were performed at 450 C for 10 hr with 100 percent fluorine flowing at a rate of 800 ml/min. The plutonium content of the initial uranium dioxide-plutonium dioxide solid solution was about 2 w/o, corresponding to the concentration that is normally present in the fluid-bed fluoride volatility process after 80 to 90 percent of the uranium has been removed. This concentration was based on the previous work by Steindler and Steidl(9) on the fluorination of mixtures of uranium and plutonium tetrafluorides, who had indicated that about 80 to 90 percent of the uranium is removed before any appreciable quantity of plutonium is volatilized. The initial solid sample contained 3 g of the inert solid and 1-2 g of the uranium dioxide-plutonium dioxide solid solution.

Table 1 lists the results obtained in these experiments. The results are expressed in terms of the uranium and plutonium contained on the inert solid after the fluorination. It will be helpful in considering these data to note that a residual concentration on the inert solid of 0.01 w/o would represent less than 0.1 percent of the original uranium and less than one percent of the original plutonium, corresponding to removal of 99.9^+ percent of the uranium and 99^+ percent of the plutonium. The economics of a one percent loss of plutonium was discussed earlier. From the data of Table 1, it is apparent that the only suitable inert solids are nickel fluoride and high-purity recrystallized alumina.

Table 1

URANIUM AND PLUTONIUM RETENTION ON INERT SOLIDS AFTER FLUORINATION

Conditions of Fluorination:

Temperature:	450 C
Fluorine Concentration:	100%
Fluorine Recycle Rate:	800 ml/min
Fluorine Pressure:	1 atm
Reaction Time:	10 hr

Inert Solid	w/o in Solid Residue U	Pu
NiF_2	0.001	0.005
Al_2O_3 (high-purity)	0.007	0.027
Al_2O_3 (Type 38)	0.017	0.108
CaF_2	0.034	0.301
AlF_3	0.060	0.180
ZrF_4	0.060	0.167

Experiments were also performed to determine the effect of reaction temperature on the retention of uranium and plutonium on alumina over the temperature range from 350 to 550 C in the same manner as those previously discussed. The results, listed in Table 2, showed that an increase in reaction temperature from 350 to 500 C produced an increase in the uranium concentration on the alumina from 0.006 to 0.011 w/o, and an increase in plutonium concentration on the alumina from 0.029 to 0.090 w/o. Although the small increase in uranium concentration on the alumina would not materially affect the economics of the process, the increase in plutonium retention from 0.029 to 0.090 w/o would seriously affect the economics of this process. Although the removals of uranium

and plutonium at 350 and 450 C were nearly identical, 450 C was selected as the reaction temperature to be used in future experiments in order to take advantage of the higher fluorination rate at the higher temperature.

Table 2

EFFECT OF FLUORINATION TEMPERATURE ON URANIUM AND PLUTONIUM RETENTION ON ALUNDUM

Fluorine Concentration: 100%
Fluorine Recycle Rate: 800 ml/min
Fluorine Pressure: 1 atm
Reaction Time: 10 hr

Temperature (C)	Residual Concentration on Al_2O_3	
	w/o U	w/o Pu
350	0.006	0.029
450	0.007	0.027
500	0.009	0.060
550	0.011	0.090

The use of one bed of inert solids for the fluorination of several batches of the dioxide mixture was studied as a possible means of minimizing the loss of plutonium on the inert solid. If the level of plutonium retention on the inert solid remained constant over several fluorinations at the value obtained after the first fluorination, a substantial reduction would be achieved in the amount of plutonium retained per batch of oxide mixture fluorinated. (The number of times that an inert bed could be reused in this manner under process conditions would depend on the degree of self-heating that would result from the accumulation of fission products.) An experiment was, therefore, performed in which the same sample of alumina was used for the fluorination of five batches of uranium dioxide-plutonium dioxide solid solution. Each fluorination was performed at 450 C for 10 hr; a small part of the residue was removed after each fluorination for analysis of uranium and plutonium. After the initial fluorination, the uranium and plutonium concentrations on the alumina were 0.009 and 0.029 w/o, respectively. The concentrations of residual uranium and plutonium on the alumina increased to values of 0.029 and 0.104 w/o, respectively, after the fluorination of the second batch, and remained nearly constant at these levels for the remaining fluorinations. The results of this experiment indicate that the recycle use of alumina would not result in an overall lower retention of plutonium than that which would have resulted if a fresh batch of alumina had been used with each of the five batches of oxide mixture. However, an economy

in the use of the inert solid and a smaller quantity of solid waste, containing a large portion of the fission products to be disposed of, would result from the recycle use of the inert solid.

The presence of fission product elements in the spent nuclear fuel might affect the removal of uranium and plutonium by fluorination. Therefore, a mixture of fission product oxides was added to the uranium-plutonium dioxide solution to determine the effect of these fission product oxides on the retention of uranium and plutonium by the inert solid. Only fission product oxides of elements that form nonvolatile fluoride were used. Table 3 lists the elements that form nonvolatile fluorides and the quantities of each that would be expected to be found in a low-enrichment uranium dioxide power reactor fuel after 10,000 Mwd/ton burnup. The values used in the table were calculated by R. K. Steunenberg.[10] The mixture of fission product element oxides employed in the fluorination studies contained the following oxides in the relative quantities shown for the elements in Table 3: BaO, ZrO_2, Y_2O_3, La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, and Gd_2O_3. The mixture of fission product oxides was blended with the uranium dioxide-plutonium dioxide solid solution prior to the fluorinations, which were carried out at 450 C for 10 hr on mixtures of 3.4 g of the solid solution (containing 3.0 g U, 0.011 g Pu, and 0.030 g F.P.) with one gram of inert solid. A similar experiment was performed with a mixture of alumina and solid solution blended with a mixture of fission product fluorides. The mixture of fission product fluorides was prepared by fluorinating a portion of the fission product oxide mixture.

Table 3

AMOUNTS OF FISSION PRODUCT ELEMENTS FORMING NONVOLATILE FLUORIDES EXPECTED IN THE PROCESSING OF A SPENT DRESDEN-TYPE FUEL[a]

Fission Product Element	Grams of Elements Per 100 Kilograms Uranium[b]
Rb	19.02
Sr	32.96
Y	20.84
Zr	154.80
Rh	23.08
Pd	11.84
Ag	0.54
Cd	1.52
In	0.30
Cs	131.00
Ba	59.60
La	48.60
Ce	88.20
Pr	41.60
Nd	170.00
Pm	3.62
Sm	39.40
Eu	1.72
Gd	0.40
	Totals 849.04

[a] 10,000 Mwd/ton burnup, 4 yr in reactor, 30-day cooled.

[b] Process mixture (2-day production) to be used initially in fluorination step: 100 kg U (as UO_2), 0.4 kg Pu (as PuO_2), 30 kg Al_2O_3, 0.88 kg fission product elements as their respective oxides.

Table 4 lists the results obtained for these experiments. Included in the table are values for experiments in which no fission products were present. The data indicate that the presence of fission product oxides in the solid solution resulted in an increased retention of plutonium but not of uranium on both alumina and nickel fluoride inert solids. The plutonium retention increased from 0.027 to 0.065 w/o on alumina and from 0.005 to 0.366 w/o on nickel fluoride. However, in the experiment in which the fission product fluoride mixture was used, the plutonium retention on alumina was reduced to

0.017 w/o, a value which is somewhat lower than the former level of 0.027 w/o. These results appear to indicate that some interaction occurs between the fission product element oxides, the plutonium oxide, and the alumina during the fluorination period.

Table 4

EFFECT OF ADDITION OF FISSION PRODUCTS ON THE RETENTION OF URANIUM AND PLUTONIUM ON INERT SOLIDS

Temperature: 450 C
Reaction Time: 10 hr

Inert Solid	Fission Products	Residue w/o U	Residue w/o Pu
Al_2O_3	None[a]	0.006	0.027
Al_2O_3	Oxides[b]	0.009	0.065
Al_2O_3	Fluorides[c]	0.006	0.017
NiF_2	None[a]	0.001	0.005
NiF_2	Oxides[b]	0.003	0.366

[a]See Table 1.

[b]Fission product mixture contained: BaO, ZrO_2, Y_2O_3, La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, and Gd_2O_3.

[c]Fission product mixture was prepared by fluorination of the oxide mixture.

Exploratory fluorinations were performed at 450 C for 5 hr with mixtures containing plutonium dioxide and individual oxides or fluorides of some of the fission product elements. The results obtained by X-ray diffraction and chemical analysis of the solid products from these experiments indicated that solid solutions formed between plutonium tetrafluoride and zirconium tetrafluoride and between plutonium tetrafluoride and cerium tetrafluoride. The analysis also indicated that compounds were formed between plutonium tetrafluoride and the fluorides of barium and cesium: $BaPuF_6$ (isostructural with $BaUF_6$), and Cs_2PuF_6 (the compound Cs_2PuCl_6 is known). The fission product element oxides, such as La_2O_3 and Nd_2O_3, which form trifluorides, did not show any indication of interaction with plutonium.

Two procedures were tried in an effort to recover additional amounts of the plutonium retained on the inert solid after a 10-hr fluorination at 450 C: The first procedure employed pyrohydrolysis of the residue at 1000 C, followed by refluorination at 450 C for 10 hr; the second employed refluorination of the residue at 550 C for a 10-hr period. As shown in Table 5, pyrohydrolysis-refluorination or the refluorination alone at 550 C reduced the plutonium content of the alumina to 0.020 w/o or less. In the case of nickel fluoride, however, the pyrohydrolysis-refluorination procedure only succeeded in reducing the plutonium content of the nickel fluoride to 0.177 w/o from the original value of 0.366 w/o. On the basis of these results, it appears that a refluorination step at 550 C for 10 hr will reduce the plutonium content of alumina to a satisfactory level of about 0.02 w/o. These results also show that nickel fluoride is not a suitable inert solid for process use.

Table 5

THE REMOVAL OF PLUTONIUM FROM FLUORINATION RESIDUES BY PYROHYDROLYSIS AND/OR REFLUORINATION

Pyrohydrolysis:	1000 C, 3 hr
Fluorination Time:	10 hr
Fluorine Recycle Rate:	800 ml/min
Fluorine Pressure:	1 atm
Fluorine Concentration:	100%

Temp (C)	Residue Pyrohydrolyzed	Inert Solid	w/o Pu in Inert Solid	
			Initial	Final
450	Yes	Al_2O_3	0.287	0.018
450	Yes	NiF_2	0.366	0.177
550	No	Al_2O_3	0.105	0.010

A method proposed for the decladding of uranium dioxide fuel depends upon the conversion of the dioxide to uranosic oxide (U_3O_8), which is formed as a finely divided, free-flowing powder. This conversion may be accomplished by passing air over the uranium dioxide at 450 C. If the oxidation is carried out in the lower section of a fluid-bed reactor, the uranosic oxide fines along with plutonium dioxide may then be carried by the gas stream to the upper portion of the reactor where the oxide mixture can be fluorinated.

In an alternative process, the oxidation reaction could be carried out in one reactor and the uranosic oxide-plutonium dioxide powder transported into the fluid bed of another reactor for contacting with fluorine.

Two procedures were tried in an effort to recover additional amounts of the plutonium retained on the inert solid after a 10-hr fluorination at 450 C. The first procedure employed pyrohydrolysis of the residue at 1000 C, followed by refluorination at 450 C for 10 hr; the second employed refluorination of the residue at 550 C for a 10-hr period. As shown in Table 5, pyrohydrolysis-refluorination or the refluorination alone at 550 C reduced the plutonium content of the alumina to 0.020 w/o or less. In the case of nickel fluoride, however, the pyrohydrolysis-refluorination procedure only succeeded in reducing the plutonium content of the nickel fluoride to 0.177 w/o from the original value of 0.365 w/o. On the basis of these results, it appears that a refluorination step at 550 C for 10 hr will reduce the plutonium content of alumina to a satisfactory level of about 0.03 w/o. These results also show that nickel fluoride is not a suitable inert solid for process use.

Table 5

THE REMOVAL OF PLUTONIUM FROM FLUORINATION RESIDUES BY PYROHYDROLYSIS AND/OR REFLUORINATION

Pyrohydrolysis: 1000 C, 3 hr
Fluorination Time: 10 hr
Fluorine Recycle Rate: 800 ml/min
Fluorine Pressure: 1 atm
Fluorine Concentration: 100%

Temp (C)	Residue Pyrohydrolyzed	Inert Solid	Initial	Final
450	Yes	Al_2O_3	0.287	0.018
450	Yes	NiF$_2$	0.365	0.177
550	No	Al_2O_3	0.105	0.010

A method proposed for the declad ding of uranium dioxide fuel depends upon the conversion of the dioxide to uranous oxide (U_3O_8), which is formed as a finely divided, free-flowing powder. This conversion may be accomplished by passing air over the uranium dioxide at 450 C. If the oxidation is carried out in the lower section of a fluid-bed reactor, the uranous oxide fines along with plutonium dioxide may then be carried by the gas stream to the upper portion of the reactor where the oxide mixture can be fluorinated.

In an alternative process, the oxidation reaction could be carried out in one reactor and the uranous oxide-plutonium dioxide powder transported into the fluid bed of another reactor for contacting with fluorine

Fluorination experiments were performed with uranosic oxide-plutonium dioxide mixtures prepared by oxidizing the uranium dioxide-plutonium dioxide solid solution with air for 3 hr at 450 C. The uranosic oxide-plutonium dioxide powder was mixed with 60 mesh alumina and fluorinated twice, first at 450 C and then at 550 C. The gas phase in these experiments contained about 25 v/o oxygen, since oxygen would accumulate in the gas phase to about this level as a result of the fluorination of the oxides under process conditions. For the fluorination at 450 C, the initial concentrations of fluorine, oxygen, and nitrogen in the gas phase were 10, 25, and 65 percent, respectively. For the fluorination at 550 C, the initial composition of the gas phase was 75 v/o fluorine and 25 v/o oxygen. Essentially all of the uranium and a large portion of plutonium were removed from the mixture during the first fluorination; the residual plutonium was removed during the second fluorination.

The results obtained in two series of tests are shown in Table 6. In one series, the duration of each fluorination period was 10 hr. In the other series, the first fluorination period was 2 hr and the second was 5 hr. The results of these tests show that the uranosic oxide-plutonium dioxide mixture is more readily fluorinated than is the solid solution of plutonium dioxide and uranium dioxide. Retention of 0.011 w/o of plutonium on the alumina, which corresponded to a removal of 98.7 percent of the plutonium, resulted when the total reaction time was 7 hr. When both fluorination periods were extended to 10 hr each, the retention of plutonium was 0.007 w/o, which corresponded to a removal of 99.5 percent of the plutonium contained in the solid mixture.

Table 6

FLUORINATION OF URANOSIC OXIDE-PLUTONIUM DIOXIDE

Fluorinating Gas Mixtures:	v/o F_2	v/o O_2	v/o N_2
1st Period (450 C):	10	25	65
2nd Period (550 C):	75	25	-

Gas Flow Rate: 800 ml/min
System Pressure: 1 atm

Temp (C)	Time (hr)	Residue w/o Pu	Percent of Initial Pu Removed[a]
450	10	0.007 ± 0.001	99.5[b] ± 0.1
550	10		
450	2	0.011 ± 0.005	98.7[c] ± 0.3
550	5		

[a] 3.42 g UO_2-PuO_2 (3 g U, 0.011 g Pu, 0.03 g fission product elements) were oxidized by air at 450 C for 3 hr to form the U_3O_8-PuO_2 mixture used. The U_3O_8-PuO_2 was mixed with 0.90 g of Al_2O_3.

[b] These results are average values for seven experiments.

[c] These results are average values for three experiments.

IV. SUMMARY

The experimental work described in this report was performed in support of the work that is being carried out on the development of fluid-bed fluoride volatility processes. In the conceptual flowsheet of one such process, spent uranium dioxide fuel elements, after decladding, will be fluorinated in a fluid-bed reactor to convert the uranium and plutonium to their respective hexafluorides. The laboratory work was directed toward devising a fluorination scheme to achieve the removal of uranium and plutonium as their hexafluorides from synthetic mixtures that simulated the spent reactor fuel which will be used as feed material in plant-scale operations of the fluid-bed fluorinator. Since the inert solids that will be used as fluidized media are to be discarded after use, it is economically important that methods for the optimum removal of plutonium and uranium from the inert solids be developed.

It was first demonstrated that uranium and plutonium could be removed from a solid solution of plutonium dioxide in uranium dioxide, in which the plutonium content was about 4 w/o, by fluorination at 450 C for 10 hr. A solid solution was used since this approximated the physical condition of the uranium and plutonium in the spent nuclear fuel. More than 99.9 percent of the uranium and 99 percent of the plutonium were removed during the fluorination.

Several materials were tested for use as fluidized inert solids: recrystallized alumina (Alundum), nickel fluoride, zirconium tetrafluoride, aluminum fluoride, and calcium fluoride. Of these materials, high-purity alumina and nickel fluoride showed the most promise. The alumina retained 0.01 w/o uranium and 0.03 w/o plutonium, whereas the nickel fluoride retained less than 0.01 w/o of each of uranium and plutonium.

The effect of reaction temperature on the retention of uranium and plutonium on alumina was examined over the temperature range from 350 to 550 C. Uranium retention on alumina increased slightly from a value of 0.006 w/o at 350 C to 0.011 w/o at 550 C. Plutonium retention on alumina, however, increased from a value of 0.029 w/o at 350 C to 0.090 w/o at 550 C.

When a mixture of 10 fission product element oxides* which form nonvolatile fluorides was added to the uranium dioxide-plutonium dioxide solid solution, increased retention of plutonium on the inert solid resulted. For alumina, the plutonium retention was increased from 0.027 to 0.065 w/o of the residue; for nickel fluoride, the plutonium retention was increased from 0.005 to 0.366 w/o of the residue. The addition of the same fission product elements as fluorides did not result in an increase in plutonium retention on the alumina.

*BaO, ZrO_2, Y_2O_3, La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, and Gd_2O_3.

Reduction of the plutonium retained on the alumina after fluorination to less than 0.02 w/o can be accomplished effectively by either of two additional treatments of the residue. One involves a pyrohydrolysis of the residue at 1000 C followed by a refluorination at 450 C for 10 hr. The other involves a refluorination at 550 C for 10 hr.

Experiments were also performed to determine the feasibility of using the same batch of alumina as the inert solid for the fluorination of several batches of a solid solution of uranium dioxide-plutonium dioxide. The recycle use of alumina in the fluorination of five batches of the solid solution did not result in a greater removal of plutonium than that which would have resulted if a separate batch of alumina had been used in each fluorination.

Experiments were performed in which the solid solution of plutonium dioxide in uranium dioxide was oxidized prior to fluorination. The oxidation resulted in a powdered mixture of uranosic oxide and plutonium dioxide. Fluorination of this oxide mixture in alumina resulted in the removal of essentially all the uranium in a reaction time of 2 hr at 450 C with 10 v/o fluorine. When this fluorination was followed by a second fluorination period of 5 hr at 550 C with 75 v/o fluorine, the plutonium content of the alumina was 0.011 w/o. When both fluorination periods were extended to 10 hr each, the retention of plutonium was 0.007 w/o, which corresponded to a removal of 99.5 percent of the plutonium contained in the solid mixture.

Future work on the fluorination of mixtures of uranosic oxide and plutonium dioxide will be performed in a $1\frac{1}{2}$-in.-diameter fluid-bed reactor. Before starting work with an oxide mixture containing plutonium, experiments will be performed with only uranosic oxide. Work with plutonium will begin after the fluid-bed apparatus has been tested and the experimental conditions have been defined.

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VI. BIBLIOGRAPHY

1. Jonke, A. A., Fischer, J. and Mecham, W., Fluoride Volatility Processing of Low Enriched Fuels, Trans. Am. Nuclear Soc., 4(2), 184-185 (1961).

2. Trevorrow, L., Fischer, J. and Riha, J., Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride by Thermal Decomposition, Trans. Am. Nuclear Soc., 5(2), 457 (1962). See also ANL-6742 (June 1963).

3. Trevorrow, L. E., Shinn, W. A. and Steunenberg, R. K., The Thermal Decomposition of Plutonium Hexafluoride, J. Phys. Chem., 65, 398-403 (1961).

4. Fischer, J., Trevorrow, L. and Shinn, W., The Kinetics and Mechanism of the Thermal Decomposition of Plutonium Hexafluoride, ibid., 65, 1843-1846 (1961).

5. Fischer, J., Trevorrow, L., Vogel, G. and Shinn, W., Plutonium Hexafluoride Thermal Decomposition Rates, Ind. Eng. Chem., Process Design Develop., 1(1), 47-51 (1962).

6. Wilson, A. S., Uranium Dioxide-Plutonium Dioxide Ceramics, HW-55319 (1958).

7. Malecha, R. F., Smith, H. O., Schraidt, J. H., Natale, J. V., Ross, N. E. and Brown, H. O. Jr., "Low Cost Gloveboxes," Proceedings of the Eighth Conference on Hot Laboratories and Equipment, TID-7599, 485-493 (1960).

8. Kessie, R. W., The Design and Construction of Thermal Flowmeters, ANL-6531 (March 1962).

9. Steindler, M. J., and Griffin, H., "Reaction of PuF_4-UF_4 Mixtures and Elemental Fluorine," Chemical Engineering Division Summary Report for Oct, Nov, Dec, 1959, ANL-6101.

10. Steunenberg, R. K., Private communication, Preliminary ADF Process Flowsheets for Commonwealth Edison Reactor Fuel, February 2, 1959.